Rates of Indole - Phenalenone Reactions in Middle Distillate Fuel

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ABSTRACT

Although reactions of indole species with phenalene species have been postulated as contributing to sediment formation upon ageing of distillate fuels, no evidence has been found for reaction of phenalenone species in accelerated ageing of fuels by the oxygen overpressure technique or higher temperature ageing. Most indole species, either from chemical sources or from methanol extracts of LCO (MELCO), were found to react under all experimental conditions, even in experiments in which no sediment was produced. Addition of either indole or 2-methylindole to MELCO/straight run distillate mixtures produced considerably more particulate matter on ageing, whereas no additional particulate was formed by addition of 3-methylindole. The results would support formation of indole/phenalene particulate in aged fuels by reaction of phenalene and alkyl substituted phenalenes with the 3-position of alkylindoles.

INTRODUCTION

Reactions between alkylindoles and phenalenones have been postulated to be a significant factor in the formation of sediments in middle distillate fuels.[1] Alkylindoles have also been reported to decrease in concentration during the ageing of fuel containing light cycle oil (LCO).[2] In studies of sediments formed from ageing of distillate fuels from Australian refineries,[3] although species associated with reaction products of alkylindoles with phenalenone were identified in the sediments, in all cases the concentration of phenalenones increased in the ageing fuel mixture. The increases in the concentration of phenalenones is undoubtedly associated with the oxidation of phenalenes present in the LCO.[4] However, as the concentration of phenalenones also increase in the ageing of fuels containing LCO, their specific role in sediment formation remains speculative.

This study was undertaken primarily to investigate the role of phenalenones in the formation of sediments. As a secondary objective, a limited study was also undertaken of the rates of reactions of alkylindoles. Two approaches were used for this investigation. The first was the addition of phenalenone, indole or methylindoles to blends of straight run distillate (SRD) or to 30% LCO/SRD blends followed by accelerated ageing of the mixture. Secondly, polar solvent extraction of LCO was undertaken as a means to separate the polar species containing heteroatoms from the less polar hydrocarbons. The extracts were then added to SRD as means of simulating the presence of LCO in SRD while minimizing the oxidation of phenalenes to phenalenones.

EXPERIMENTAL

Experimental fuel samples were obtained directly from automotive distillate streams of Australian refineries. Experiments in Table 1 were done with SRD from refinery A,[3] while those in Table 3 were done with SRD from refinery G. They were stored at -12°C upon receipt from the refinery, which was within one week of production. Immediately before being used for the experiments described in this presentation, the samples were thawed, blended and filtered through Millipore AP40 glass fibre filters. Pairs of these filters were used for sediment determination by the method of ASTM D4625. Sediment determination were done in duplicate for model compound additives and the average of the two results shown in the Table 1. Results in Table 3 are for single determinations only.

Commercial samples of indole, 2-methylindole and para-toluenesulphonic acid monohydrate from Fluka Chemika and 3-methylindole and phenalenone (perinaphthenone) from Aldrich Chemicals were used directly as received.

Polar extracts of LCO were obtained by shaking 500 ml of the LCO from refinery F[3] with 5 x 100 ml portions of methanol. The methanol extracts were combined and stored at -12°C. Prior to ageing experiments, measured portions of the methanol extract were evaporated to dryness under vacuum at ambient temperature. The residue was then dissolved in the experimental fuel blend.

Most accelerated ageing studies were carried under oxygen overpressure conditions[5] using the single bomb apparatus of ASTM D942 at a oxygen pressure of 794 kPa and temperature of 95°C as outlined elsewhere.[6] These conditions for an ageing time of 64 hours will be referred to as OP conditions in the remainder of the paper. Studies were also carried out at atmospheric pressure in a thermostated air oven using 700 ml of fuel in loosely capped 1 litre borosilicate flasks.

Phenalenone and indole determinations were performed on the experimental fuel blends prior to and after fixed ageing periods. Determination of phenalenones was performed by high pressure liquid chromatography using a Waters 5 um spherical silica column of 150 mm length and 4.6 mm diameter at ambient temperature. All phenalenones were eluted under isocratic conditions with a 9:1 mixture of heptane with chloroform containing 1.5% propan-2-ol. Following elution of the phenalenones, the column was flushed with propan-2-ol prior to the next run. The phenalenones were detected by serial detectors at wavelengths of 384 nm and 254 nm. Good agreement was obtained between the two wavelengths after standardization with 0-1000 umol/L solutions of phenalenone in the eluent, indicating the minimal co-elution of interfering substance with the phenalenones. Indoles were determined by gas chromatography using a nitrogen specific detector as described elsewhere.[6] Thin layer chromatography (TLC) of sediments were performed on Merck HPTLC Silica Gel 60 F254 plates using a 10% methanol/dichloromethane solvent.[6]

RESULTS AND DISCUSSION

Ageing of samples of SRD alone produces very little sediment, but upon admixture of LCO with the SRD, significant amounts of sediment are produced.[7] Phenols[6], phenalenones[1], alkylindoles[1,2], and acids[7,9] have all been postulated to be precursors for sediment formation. A reference sample of SRD was aged for the equivalent of 3-5 years ambient ageing under the vigorous conditions of the oxygen overpressure test[5] for 64 hours at 95°C with a pressure of 794 kPa oxygen. Both phenalenone and indole then were added to the SRD at concentrations of 588 umol/L and 981 umol/L respectively. These are equivalent to concentrations at the upper end of those measured for phenalenone and alkylindoles in 30% LCO/SRD blends.[3] As may be seen from Table 1, no additional sediment was formed in the fuel containing the additives on ageing.

The results would also suggest that species which catalyse the reactions of indole with phenalenone are not formed from stressing of the SRD under the OP conditions. In particular, the acid species which would be expected to be formed,[9] do not act as a catalyst. In order to investigate the effect of strong acids further, a saturated solution at 20°C of para-toluenesulphonic acid monohydrate in SRD containing indole and phenalenone as previously was prepared and aged under the OP conditions. This acid is known to be effective in promoting sediment formation in fuel containing LCO.[7] No additional sediment was formed compared to SRD without additives. It may be concluded that the concentration of p-toluenesulphonic acid dissolving at 20°C in combination with acid produced by OP ageing of the SRD is insufficient to promote reaction between the indole and phenalenone in the SRD.

The experiments were then repeated with a fuel mixture of 30% LCO in SRD. This mixture produced 67 mg/L sediment under the OP conditions without the addition of additives. Phenalenone and indole were added and the fuel aged. The amount of sediment increased to 125 mg/L. Phenalenone was then added to the 30% LCO/SRD fuel without any indole. The amount of sediment formed after OP ageing at 63 mg/L was the same within the experimental error as that produced from the reference 30% LCO/SRD blend. Finally, for these series of experiments shown in Table 1, indole without phenalenone was added to the reference fuel. The amount of sediment of 122 mg/L formed after OP ageing was the same as that produced for fuel containing both phenalenone and indole.

The effect of methyl substitution upon the indole nitrogen containing ring was then investigated. The addition of 2-methylindole to the 30% LCO/SRD fuel mixture produced 157 mg/L sediment after OP ageing, whereas the addition of 3-methylindole resulted in only 60 mg/L of sediment. Increased sediment is formed from 2-methylindole compared to indole itself, whereas 3-methylindole does not produce any additional sediment compared to the undoped fuel. These results would suggest that reaction of the indole molecule to form sediments is via the 3-position. The 2-methyl substituent facilitates reaction at the 3-position, whereas the 3-methyl group blocks the reaction.

The results may be compared with the effect upon sediment formation of the presence of both 3-methylindole and tert-butylhydroperoxide in shale derived fuels.[10] Significantly increased sediment formation was observed when both additives were present. It may be concluded that sediment formation from 3-methylindole in the presence of tert-butoxy radicals is predominantly a free radical process. Hindered phenols act as effective free radical traps, but are known to be ineffective in reducing sediment formation in unstable fuels.[11] As no evidence was found for the reaction of the 3-methylindole under the OP conditions of this work, it may be concluded that the OP conditions are more comparable to ambient ageing than those in the presence of free radical promoters.

TLC analyses of the sediments were undertaken to compare sediments produced from the 30% LCO/SRD mixture in the presence and absence of additives. These are shown schematically in Table 2. Thin layer chromatograms of sediments from the reference fuel without additives, and from that containing either phenalenone or 3-methylindole were identical within experimental error, confirming that these additives had not contributed to the sediments. Only sediment from the reference fuel is shown in Table 2. The major feature of the thin layer chromatograms of sediment from the indole additive was the increased prominence of a blue material at approximate R_f 0.25 to 0.35. With the 2-methylindole additive this blue material was very intense. It is postulated to be the acid salts of alkylindolylphenalenes

Direct measurements of indole concentrations were not done for the experiments in Table 1. Indole concentrations that are shown are those which were added to the solution. In a second series of experiments, direct measurements of indole concentrations were made before and after ageing.. For these experiments shown in Table 3, methanol extracts of LCO from refinery F were also added to SRD from refinery G. This combination was used due to the relatively high indole content of the LCO for refinery F[3] and the water white nature of SRD from refinery G.

Ageing of the SRD under the OP conditions used previously produced 10 mg/L total particulate from the SRD. Similar ageing of the SRD with added indole, both with and without added phenalenone, produced the same amount of sediment as the SRD alone within the experimental error. The indole and phenalenone concentrations were measured in the solution after ageing as shown in Table 3. The final phenalenone concentration was unchanged from that initially and consistent with no additional sediment being formed in the presence of the phenalenone. However, although no additional sediment was formed in either solution in the presence of added indole, in both cases the concentration of indole had decreased to approximate half its original value. These results clearly indicate a non-particulate forming reaction of the indole in the SRD.

Ageing of SRD containing methanol extracts of LCO produced 89 mg/L of sediment. The addition of 490 umol/L of phenalenone to the solution prior to ageing did not produce any change in the amount of sediment formed. The results are comparable with those of Hardy and Welcher,[12] who found that ageing methanol extracts of LCO in hydrocarbons produced sediments of similar mass to that produced from the equivalent volume of unextracted LCO. As with the experiments discussed in the previous paragraph, the total indole concentration (in the case of the extract it is a mixture of many alkyl indoles[3]) decreased considerably in the aged solution, whereas the phenalenone concentration was unchanged after ageing.

The ageing of the methanol extract in SRD was repeated with an air atmosphere in an thermostated oven. Both the initial total alkylindole and phenalenone concentration was low at 270 and 4 umol/L respectively and only 6 mg/L of sediment was formed after 14 days ageing at 80°C. The addition of 780 umol/L of phenalenone to the reference solution resulted in the formation of 7 mg/L of sediment, unchanged within the experimental error. Again there was a significant reduction in the final total indole concentration, but none in the final phenalenone concentration. Finally, a greater concentration of methanol extract in SRD was aged with an air atmosphere for 65 hours at 120°C. After this period, 41 mg/L of sediment had been formed and the total alkylindole concentration had decreased to one fifth of its original value, but the phenalenone concentration was unchanged at 28 umol/L. Not only was the unsubstituted phenalenone concentration unchanged after ageing at the elevated temperature, but so were all other substituted phenalenones as detected in the HPLC chromatogram at a detector wavelength of 384 nm as shown in the chromatograms before and ageing in Figure 1. Although these other species have not been definitively identified as phenalenones, the HPLC retention time and absorption at 384 nm is indicative of the phenalenone chromatophore.

If phenalenone species do not react with indoles in SRD under the severe ageing conditions used in this work, it may be concluded that it is unlikely that they react at ambient temperatures. However, blue and pink materials observed in the thin layer chromatograms of the sediments from this and previous work has been postulated to be acid salts of alkylindolylphenalenes and alkylindolylphenalenones.[1,6] It is proposed that the acids salts arise following reactions between alkylindoles with unoxidized phenalene species to form indolylphenalenes which may subsequently oxidized to indolylphenalenones as shown in Figure 2. Phenalenes have been shown to be present in relatively high concentrations in LCO.[4] The large increase in blue material observed in the thin layer chromatogram of sediment formed upon ageing when 2-methylindole is added to fuel mixture containing LCO follows from coupling with phenalenes at the favoured 3-position of the alkylindoles. This coupling is blocked in the case of 3-methylindole.

CONCLUSIONS

No evidence has been found for reaction of phenalenone species under conditions of oxygen overpressure and elevated temperature ageing of SRD containing either indole and phenalenone as model compounds or these species present from methanol extracts of LCO. Indole species were found to react under all the experimental ageing conditions. Although approximately 50% of indole in SRD aged under OP conditions of 64 hours at 95°C was found to have reacted, no additional particulate matter was formed in the fuel.

Particulate matter was formed on ageing when solid residue from methanol extracts of LCO were added to SRD. The total alkylindole concentration in the SRD/extract mixture decreased by at least 50% during the ageing experiments. However, in none of the experiments was any decrease in phenalenone concentration recorded. No additional particulate matter was formed when phenalenone was added to SRD/extract mixture.

Addition of either indole or 2-methylindole to the extract/SRD mixture resulted in considerably more particulate matter being produced. No increase in particulate was found when the SRD/extract mixture containing 3-methylindole was similarly aged.

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FUEL	INDOLE ADDED umol/L	PHENALENONE ADDED umol/L	TOTAL PARTICULATE mg/L
SRD	0	0	17
SRD	981	588	14
30% LCO/SRD	0	0	67
30% LCO/SRD	793	604	125
30% LCO/SRD	0	627	63
30% LCO/SRD	972	0	122
30% LCO/SRD	754[a]	0	157
30% LCO/SRD	792[b]	0	60

a as 2-methylindole
b as 3-methylindole

Table 1. Total sediment formed after oxygen overpressue ageing at 794 kPa for 64 hours at 95°C of fuel from Refinery A.

R_f RANGE	BAND COLOUR	NO ADDITIVES	INDOLE ADDED	2-METHYLINDOLE ADDED
1.00-0.96	green	L	L	L
0.94-0.87	orange	L	M	D
0.74-0.73	green	VL	NO	VL
0.72-0.71	grey	VL	NO	VL
0.55-0.43	pink	M	L	M
0.42-0.26	blue	L	D	VD
0.26-0.22	orange	VL	M	NO
0.21-0.25	yellow	NO	M	NO
0.08-0.04	brown	L	M	M

NO not observed
VL very light
L light
M medium
D dark
VD very dark

Table 2. Thin layer chromatogram schematics of sediment from 30% LCO/SRD fuel from refinery A.

Fuel Ageing	TOTAL ALKYLINDOLE concentration Initial umol/L	Final umol/L	PHENALENONE concentration Initial umol/L	Final umol/L	TOTAL PARTICULATE MATTER mg/L
a	0	0	0	0	10
b	1072	497	0	0	14
c	1072	562	99	95	12
d	1613	921	21	28	89
e	1613	593	511	512	88
f	270	85	4	4	6
g	270	80	786	800	7
h	2555	506	28	29	41

a SRD reference fuel OP aged (64 hr at 95°C with 794 kPa oxygen)
b SRD + added indole OP aged
c SRD + added indole and phenalenone OP aged
d SRD + LCO extract OP aged
e SRD + LCO extract and added phenalenone OP aged
f SRD + LCO extract aged for 336 hr at 80°C
g SRD + LCO extract and added phenalenone aged for 336 hr at 80°C
h SRD + LCO extract aged for 65 hours at 120°C

Table 3. Variation of total alkylindole and phenalenone concentrations and total particulate on ageing SRD containing methanol extracts of LCO with and without added phenalenone.

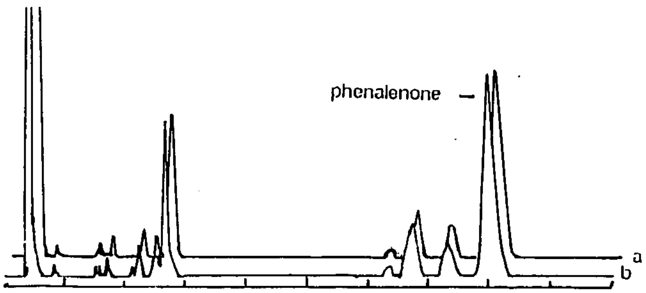

Figure 1. HPLC Chromatogram of absorption at 384 nm for SRD containing methanol extract of LCO, (a) before and (b) after ageing at 120°C for 65 hours.

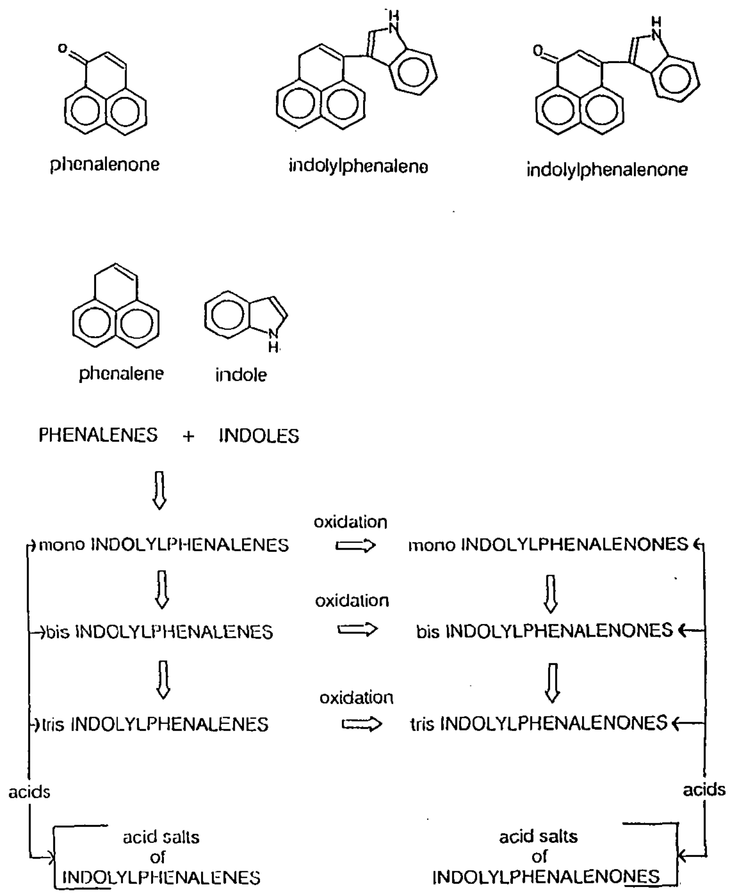

Figure 2. Possible Reaction schematic for formation of particulate from reaction of indole and phenalenone species.